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Proton Transfer in Water Polymers as a Model for Intime and Solvent-Separated Ion Pairs

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SCF-CNDO/2 calculations, including the continuum solvent effects via an extended version of the generalized Born formula, have been performed for $\text{H}_3\text{O}^+\cdots(\text{H}_2\text{O})_n\cdots\text{OH}^-$ and $(\text{H}_2\text{O})_n\cdots\text{H}_3\text{O}^+\cdots\text{OH}^-$ species ($n = 0, 1, 2$). The proton potential curves were calculated by both varying the position of one of the intervening protons and varying the positions of all of them simultaneously, in a chain of water molecules. The oxygen and remaining hydrogen atoms were kept fixed at several intermolecular distances. By these procedures an intime ion-pair structure and a one- and two-solvent-separated ion-pair structure were respectively generated. Qualitative results show a stabilization of the intime ion-pair structure with respect to the solvent-separated one. This effect is even more pronounced when additional water molecules are incorporated into the chain.

Introduction

In the past few years, great effort has been devoted to the study of proton-transfer reactions.¹⁻⁴ For these systems, experimental

results suggested the participation of intermediate complexes presenting intime or solvent-separated ion-pair structures.⁵⁻⁷ The stabilization of such ionic structures results from interaction with

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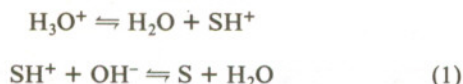
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an appropriate environment. Although an important number of quantum-mechanical studies have been devoted to this problem,⁸⁻¹⁰ continuum (or dielectric) solvent effects have not been considered explicitly. This effect together with specific interactions with the solvent may be important in discussing which of these ionic structures should be expected in a particular chemical reaction.

Since a great number of chemical reactions occur in aqueous solution, we propose to study the proton transfer in water polymers as a model to characterize the properties of this solvent with regard to the function of intimate or solvent-separated ion pairs. The study of the free energy profile for proton transfer, taking into account both local and continuum solvent effects, may provide some valuable information about this problem.

The explicit participation of the solvent in the proton-transfer process in water polymers has been discussed by Eigen et al.¹¹ Two kinds of stepwise mechanisms were proposed. The first one may be represented by



where the solvent ($\text{S} = \text{H}_2\text{O}$ in this case) appears to play a key role. In the second one, the proton is transferred directly from H_3O^+ to OH^- . Recently, an alternative mechanism, which involves a simultaneous transfer of the proton along a chain of water molecules between the H_3O^+ and the OH^- , has been proposed by Busch et al.¹⁰

From Eigen's mechanism, the formation of an intimate ion-pair structure which could be stabilized by interaction with the highly polarizable medium may be envisaged. If the proton transfer occurs via a mechanism such as that proposed by Busch et al., a solvent-separated ion-pair structure may then be envisaged.

In this work, we present calculations on the free energy changes that take place when the proton is transferred from the donor molecule to the acceptor molecule at several intermolecular distances, in the presence of a strongly polarizable medium. Five systems have been considered: (1) the proton transfer between two water molecules (an intimate $(\text{H}_3\text{O}^+, \text{OH}^-)_e$ ion pair is so generated); (2) the transfer of one proton in a planar trimer arrangement which leads to an intimate $(\text{H}_2\text{O} \cdot \text{H}_3\text{O}^+, \text{OH}^-)_e$ ion-pair structure; (3) the simultaneous transfer of the two intervening protons in a planar trimer arrangement in order to generate a one-solvent-separated $(\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_2 \cdot \text{OH}^-)_e$ ion-pair structure; (4) the transfer of one proton in a planar tetramer arrangement leading to an intimate $((\text{H}_2\text{O})_2 \cdot (\text{H}_3\text{O}^+, \text{OH}^-))_e$ ion-pair structure; (5) the simultaneous transfer of all the intervening protons in a planar tetramer arrangement leading to a two-solvent-separated $(\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_2 \cdot \text{OH}^-)_e$ ion-pair structure.

The corresponding geometries with their respective geometrical parameters are shown in Figure 1.

Method of Calculation

Self-consistent-field calculations including continuum solvent effects were performed within the CNDO approximation. Solvent effects were incorporated by using an extended version of the generalized Born formula. This model allows the inclusion of steric hindrance effects upon solvation of each atomic center of the solvated molecular system. In this approach, the total free energy of the solute-solvent system is given by the following expression:¹²

$$A(\epsilon, P) = E(1, P) + \Delta A(\epsilon, P) \quad (2)$$

where ϵ is the macroscopic dielectric constant and P the one-

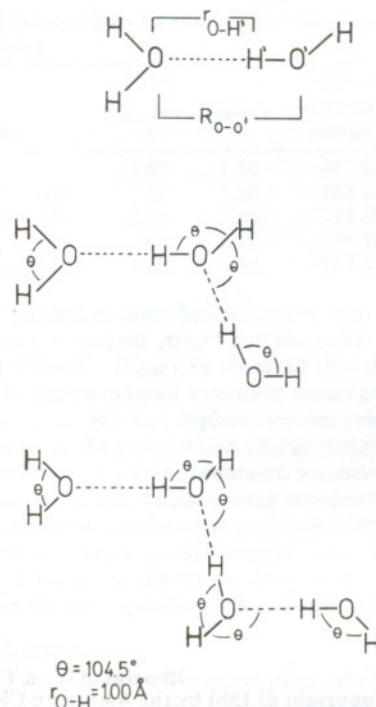


Figure 1. Structure and geometrical parameters for proton transfer in water polymers.

particle density matrix. The solvation free energy $\Delta A(\epsilon, P)$ is calculated in terms of the electrostatic solute-solvent interaction energy $E_{\Sigma-S}(\epsilon, P)$ as¹²

$$\Delta A(\epsilon, P) = \frac{1}{2} E_{\Sigma-S}(\epsilon, P) = \frac{1}{2} \sum_A Q_A(P) [{}^i V_R(\epsilon, P) + {}^e V_R(\epsilon, P)]_A \quad (3)$$

where

$${}^i V_R(\epsilon, P)_A = \sum_B {}^i Q_B^{\text{Pol}}(P) {}^i \gamma_{AB} \quad (4)$$

$${}^e V_R(\epsilon, P)_A = \sum_B {}^e Q_B^{\text{Pol}}(P) {}^e \gamma_{AB} \quad (5)$$

are the internal and external contributions to the reaction field potential created on each atomic center of the solute molecule by the internal and external polarization charges

$$\begin{aligned} {}^i Q_B^{\text{Pol}}(P) &= \alpha(\epsilon)(1 - f_B) Q_B(P) = \\ &= -(1 - 1/\epsilon)(1 - f_B) [Z_B - \sum_{\nu} P_{\nu\nu}] \\ &\quad \nu \in B \end{aligned} \quad (6)$$

$$\begin{aligned} {}^e Q_B^{\text{Pol}}(P) &= \alpha(\epsilon) f_B Q_B(P) = -(1 - 1/\epsilon) f_B [Z_B - \sum_{\nu} P_{\nu\nu}] \\ &\quad \nu \in B \end{aligned} \quad (7)$$

respectively. f_B is a parameter characterizing the specific neighborhood effects upon the B-atomic center (i.e., steric hindrance effects upon the solvation of the B-atomic center). This parameter is represented empirically by¹²

$$f_B = \frac{1}{2} \sum_{A \neq B} S_{AB} \quad (8)$$

where S_{AB} is the overlap integral between the $2s_A$ and $2s_B$ atomic orbitals (1s for hydrogen atoms). The quantities ${}^i \gamma_{AB}$ and ${}^e \gamma_{AB}$ are the internal polarization charge-electron and external polarization charge-electron interaction integrals, respectively. They are related to the habitual CNDO/2 γ_{AB} matrix by

$${}^i \gamma_{AB} = (1 - f_B)_{AB} \quad {}^e \gamma_{AB} = f_B \gamma_{AB} \quad (9)$$

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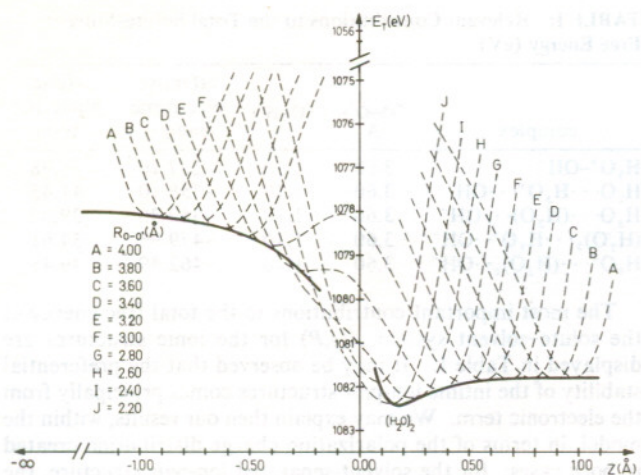


Figure 2. Proton transfer in water dimer ($\epsilon \rightarrow \infty$): (---) proton potential curves for $(\text{H}_2\text{O})_2$ system, (—) reaction path profile for $(\text{H}_2\text{O})_2$ system.

respectively. Within this approach, the solvation free energy is given by

$$\Delta A(\epsilon, P) = -\frac{1}{2}(1 - 1/\epsilon) \sum_A \sum_B Q_A(P) Q_B(P) (1 - F(S)) \gamma_{AB} \quad (10)$$

where $F(S) \geq 0$ depends on the S matrix only. $\Delta A(\epsilon, P)$ is then the generalized Born formula^{13,14} corrected by a desolvation contribution $\Delta A(\epsilon, P)$ ¹²

$$\Delta A^{\text{des}}(\epsilon, P) = \frac{1}{2} \sum_A \sum_B F(S) Q_A(P) Q_B^{\text{Pol}}(P) \gamma_{AB} \quad (11)$$

Results and Discussion

The results of our calculation on the free energy changes for proton-transfer processes between water molecules at several intermolecular distances are displayed in Figures 2–5. The continuum solvent effect was included via the extended Born formula (EBF) according to eq 10. In order to represent in the simplest way the total free energy variations, we have defined the reduced coordinate $Z = r_{\text{O-H}'} - \frac{1}{2}R_{\text{O-O}'}$, where the $r_{\text{O-H}'}$ and $R_{\text{O-O}'}$, geometrical parameters are conveniently defined in Figure 1. This reduced coordinate defines the position of the proton for different $R_{\text{O-O}'}$ distances.

The proton-transfer free energy curves for the water dimer are shown in Figure 2. It may be seen that for $R_{\text{O-O}'}$ distances greater than 2.80 Å, the proton is transferred within a double-minimum pathway: one corresponding to an H-bonded $(\text{H}_2\text{O} \cdots \text{H}_2\text{O})_e$ neutral complex, the other corresponding to an intimate proton-transfer $(\text{H}_3\text{O}^+, \text{OH}^-)$ ion pair which appears strongly destabilized with respect to the neutral complex. Defining the reaction path profile as the trajectory passing through the minima of the proton potential curves, one may observe that the proton is transferred within a one-minimum potential corresponding to the H-bonded $(\text{H}_2\text{O} \cdots \text{H}_2\text{O})_e$ neutral complex at $R_{\text{O-O}'} = 2.40$ Å and $R_{\text{O-H}'} \sim 1.30$ Å. For $R_{\text{O-O}'} > 3.0$ Å, a metastable state corresponding to the ion-pair structure is obtained, and, as expected, it is strongly destabilized with respect to the $(\text{H}_3\text{O}^+)_e$ and $(\text{OH}^-)_e$ solvated free ions.

A similar behavior is obtained for proton transfer in water trimer and tetramer. The proton potential curves and the reaction path profile obtained for the transfer of one proton in the trimer arrangement are illustrated in Figure 3. An H-bonded $(\text{H}_2\text{O} \cdots \text{H}_2\text{O} \cdots \text{H}_2\text{O})_e$ neutral structure appears at $R_{\text{O-O}'} \sim 2.50$ Å and $r_{\text{O-H}'} \sim 1.40$ Å, followed by a metastable state at $R_{\text{O-O}'} > 3.40$ Å corresponding to an intimate $(\text{H}_2\text{O} \cdots (\text{H}_3\text{O}^+, \text{OH}^-))_e$ ion pair. In Figure 4, the proton potential curves and the reaction path profile for the simultaneous transfer of the two intervening protons are displayed. For $R_{\text{O-O}'} > 3.40$ Å, a metastable state corresponding

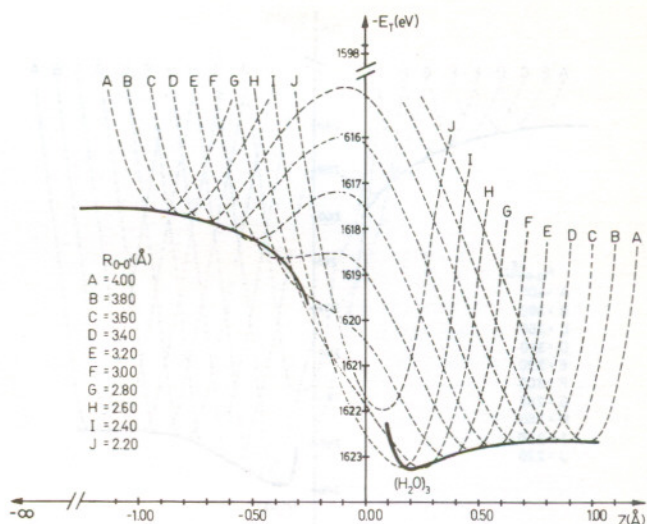


Figure 3. Proton transfer in water trimer; one proton is transferred ($\epsilon \rightarrow \infty$): (---) proton potential curves for $(\text{H}_2\text{O})_3$ system, (—) reaction path profile for $(\text{H}_2\text{O})_3$ system.

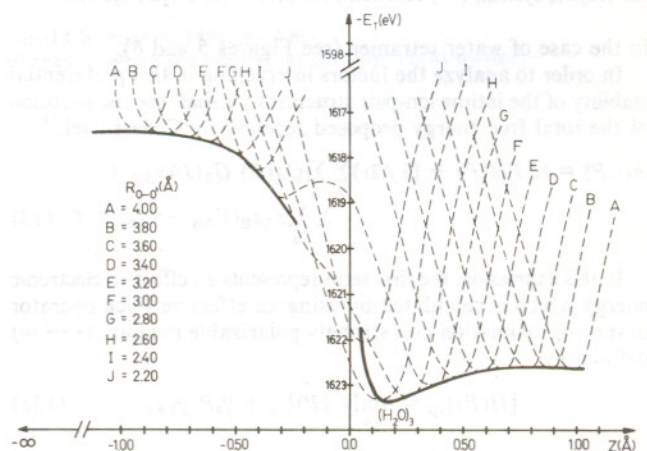


Figure 4. Proton transfer in water trimer; the two intervening protons are transferred simultaneously ($\epsilon \rightarrow \infty$): (---) proton potential curves for $(\text{H}_2\text{O})_3$ system, (—) reaction path profile for $(\text{H}_2\text{O})_3$ system.

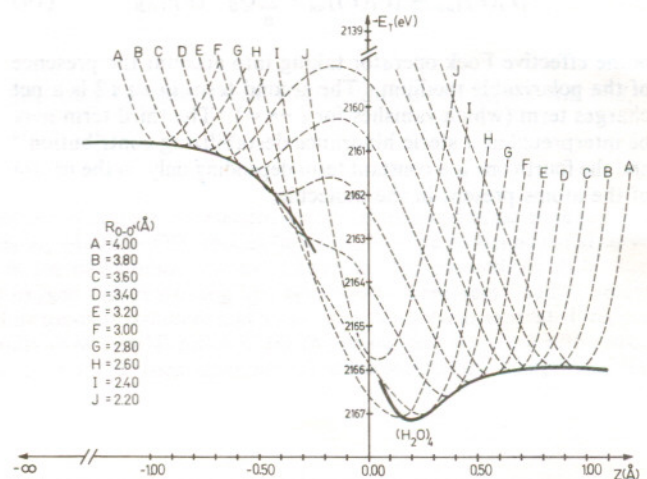


Figure 5. Proton transfer in water tetramer; one proton is transferred ($\epsilon \rightarrow \infty$): (---) proton potential curves for $(\text{H}_2\text{O})_4$ system, (—) reaction path profile for $(\text{H}_2\text{O})_4$ system.

to a "solvent-separated" $(\text{H}_3\text{O}^+ \cdots (\text{H}_2\text{O}) \cdots \text{OH}^-)_e$ ion pair is observed. By comparison of the reaction path profiles for intimate and solvent-separated ion-pair formation, a difference of ~ 0.3 eV is observed in favor of the intimate ion-pair structure. This preferential stability for the intimate ionic structure is increased

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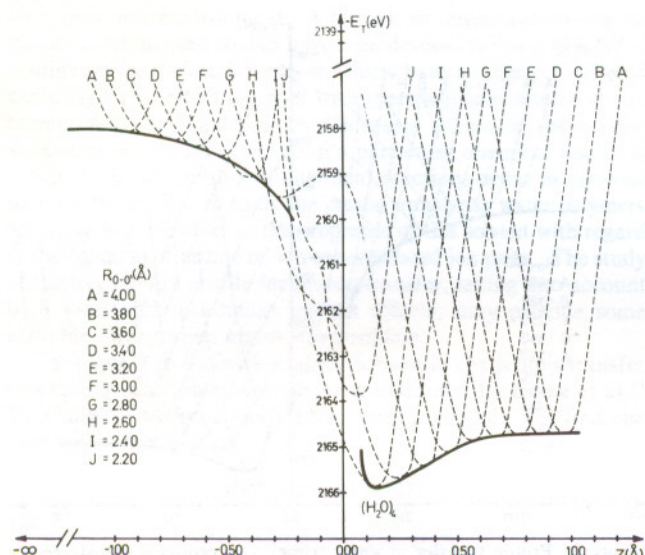


Figure 6. Proton transfer in water tetramer; the three intervening protons are transferred simultaneously ($\epsilon \rightarrow \infty$): (---) proton potential curves for $(\text{H}_2\text{O})_4$ system, (—) reaction path profile for (H_2O) system.

in the case of water tetramer (see Figures 5 and 6).

In order to analyze the factors intervening in this preferential stability of the intime ion-pair structures we shall use the partition of the total free energy proposed recently by Constanciel.¹⁴

$$A(\epsilon, P) = \text{tr } P\bar{H}(P) + (1/2\epsilon) \sum_A \sum_B Q_A(P) Q_B(P) \gamma_{AB} + \sum_A \sum_B z_A z_B (\Gamma_{AB} - \gamma_{AB}) + C \quad (12)$$

In this expression, the first term represents an effective electronic energy which is calculated by using an effective Fock operator in the approximation of a strongly polarizable medium ($\epsilon \rightarrow \infty$) defined by

$$[\bar{H}(P)]_{\mu\mu} = \lim_{\epsilon \rightarrow \infty} [F_\epsilon(P)]_{\mu\mu} + 1/4 P_{\mu\mu} \gamma_{AA} \quad (13a)$$

$$[\bar{H}(P)]_{\mu\nu} = [F_1(P)]_{\mu\nu} + 1/4 P_{\mu\nu} \gamma_{AB} \quad (13b)$$

where

$$[F_\epsilon(P)]_{\mu\mu} = [F_1(P)]_{\mu\mu} - \sum_B Q_B^{\text{Pol}}(P) \gamma_{AB} \quad (14)$$

is the effective Fock operator taking into account the presence of the polarizable medium. The second term in eq 12 is a net charges term (which vanishes for $\epsilon \rightarrow \infty$). The third term may be interpreted as a steric hindrance destabilizing contribution¹⁴ and the fourth one is a constant term depending only on the nature of the atoms present in the molecule.

TABLE I: Relevant Contributions to the Total Solute-Solvent Free Energy (eV)

complex	$r_{\text{O-O}'}$, Å	$r_{\text{O-H}'}$, Å	effective electronic energy	steric hindrance term
$\text{H}_3\text{O}^+ \cdots \text{OH}^-$	3.60	1.10	-237.10	25.98
$\text{H}_2\text{O} \cdots \text{H}_3\text{O}^+ \cdots \text{OH}^-$	3.60	1.10	-358.10	41.45
$\text{H}_3\text{O} \cdots (\text{H}_2\text{O})_2 \cdots \text{OH}^-$	3.60	1.10	-350.30	39.02
$(\text{H}_2\text{O})_2 \cdots \text{H}_3\text{O}^+ \cdots \text{OH}^-$	3.60	1.10	-479.96	54.61
$\text{H}_3\text{O}^+ \cdots (\text{H}_2\text{O})_2 \cdots \text{OH}^-$	3.60	1.10	-462.49	49.45

The most important contributions to the total free energy of the solute-solvent system $A(\epsilon, P)$ for the ionic structures are displayed in Table I. It may be observed that the preferential stability of the intime ion-pair structures comes principally from the electronic term. We may explain then our results, within the model, in terms of the polarization charge distribution created in both cases: for the solvent-separated ion-pair structure, the internal water molecules induce a weak polarization on the medium, while for the intime ion-pair structure, a stronger reaction field potential is created on each atomic center of the solvated ion pair. Consequently, the intime ion-pair structure is better solvated than the corresponding solvent-separated one.

Concluding Remarks

In summary, we have studied qualitatively the proton transfer between water molecules in the planar hydrogen-bonded system $(\text{H}_2\text{O})_n$ ($n = 0, 2, 3, 4$) in the presence of strongly polarizable medium, as a model for intime and solvent-separated ion pairs. The energetics of proton transfer shows the preferential stabilization of the intime ion-pair structure with respect to the solvent-separated one, an effect that increases with n . Although, in principle, the preferential stability of one ionic structure against the other has been attributed to the fact that a single or a simultaneous proton transfer occurs, our results show that this difference is principally due to the contribution of the solvation free energy, which is greater for the intime ion-pair structure.

Furthermore, it should be noted that recent results obtained by Scheiner on the proton-transfer study on cationic oligomers of water¹⁵ show that a simultaneous proton transfer occurs at no more cost in energy than a single-proton transfer, supporting our conclusion.

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